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Electrochemical Determination of Thermodynamic Properties of MnF_2 and CoF_2

By Seth C. Schaefer

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES 75TH ANNIVERSARY

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cal	calorie	min	minute
cal/mol	calorie per mol	mm	millimeter
cal/mV	calorie per millivolt	mol pct	mol percent
cm^3/min	cubic centimeter per minute	MPa	megapascal
h	hour	mV	millivolt
J	joule	Pa	pascal
K	kelvin	wt pct	weight percent

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ELECTROCHEMICAL DETERMINATION OF THERMODYNAMIC PROPERTIES OF MnF_2 AND CoF_2

By Seth C. Schaefer [1]

ABSTRACT

The Bureau of Mines investigated the standard Gibbs energies of formation, $\Delta Gf°$, for MnF_2 (manganese difluoride) and CoF_2 (cobalt difluoride). High-temperature galvanic cells employing CaF_2 (calcium difluoride) as the solid electrolyte were used to measure the open-circuit potentials for the cell reactions

$$Mn(c) + NiF_2(c) = MnF_2(c) + Ni(c)$$

and

$$Co(c) + NiF_2(c) = CoF_2(c) + Ni(c).$$

Combination of the standard Gibbs energy changes for these reactions with the standard Gibbs energy of formation of NiF_2 yielded the following:

$$\Delta Gf°(MnF_2) = (-203{,}008 + 30.96T) \pm 560 \quad (745.7\text{-}1{,}078.3\ K)$$

and

$$\Delta Gf°(CoF_2) = (-159{,}090 + 32.13T) \pm 420 \quad (769.5\text{-}1{,}026.8\ K),$$

where $\Delta Gf°$ is expressed in calories per mol (1 cal = 4.184 J) and T is expressed in kelvins. The standard enthalpies of formation $\Delta Hf°$, derived by the third-law method, are

$$\Delta Hf°_{298}(MnF_2) = -204{,}633 \pm 560 \text{ cal/mol}$$

and

$$\Delta Hf°_{298}(CoF_2) = -161{,}166 \pm 420 \text{ cal/mol}.$$

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INTRODUCTION

Thermodynamic properties of MnF_2 and CoF_2 were investigated by the Bureau of Mines as a part of its program to expand the base of scientific information needed to devise innovative technologies. Many chemical and metallurgical processes involve halogen gases and metal halide compounds (1).[2] MnF_2 is used in electronics, optics, and as a catalyst in hydrocarbon isomerization. CoF_2 is used as a catalyst in isomerization and polymerization reactions. A review of existing data reported in compilations (2-5) shows considerable disagreement in the Gibbs energies of formation for these compounds and suggests a need for careful investigation to resolve some of these discrepancies.

Galvanic cells with solid CaF_2 electrolyte have been used successfully to obtain Gibbs energy data for fluorides, borides, and phosphides (5-6). Extensive investigation of the electrolytic behavior of CaF_2 and CaF_2 doped with YF_3 showed that conduction is ionic and that the transport number is essentially unity (7-9), even under strongly reducing conditions. The method is based on the measurement of the difference in chemical potential of fluorine between a reference electrode of known fluorine potential and an electrode of unknown fluorine potential consisting of a metal and its coexisting fluoride or two coexisting fluorides. The relationship between the open-circuit potential of electromotive force (emf) cells and the Gibbs energy change for the actual cell reaction is

$$\Delta G(\text{reaction}) = -nFE, \qquad (1)$$

where ΔG is the change in Gibbs energy for the cell reaction, n is the number of electrochemical equivalents in the reaction, F is the Faraday constant (23.061 cal/mV equivalent), and E is the emf in millivolts. The standard states for the solids involved in the reaction are the saturated coexisting phases. Intersolubility of the two-phase electrode mixtures was determined to be negligible by X-ray diffraction analyses. Consequently, no appreciable error was introduced in the Gibbs energies for the cell reactions by assuming unit activity for the reactants and products involved in the cell reactions.

EXPERIMENTAL WORK

MATERIALS

High-purity reagents were obtained from commercial sources and used without further purification. Analyses of these reagents were confirmed and are presented in table 1. Argon of 99.999-mol-pct purity was used to provide a protective atmosphere for the cell. Single crystals of CaF_2, doped with approximately 1 mol pct YF_3 were used as the solid electrolyte.

APPARATUS AND PROCEDURE

Internal arrangement of the cell components is illustrated in figure 1. A detailed description of the cell and experimental procedure was previously published (10). Similar cell designs have been reported in the literature (5-6, 11-12).

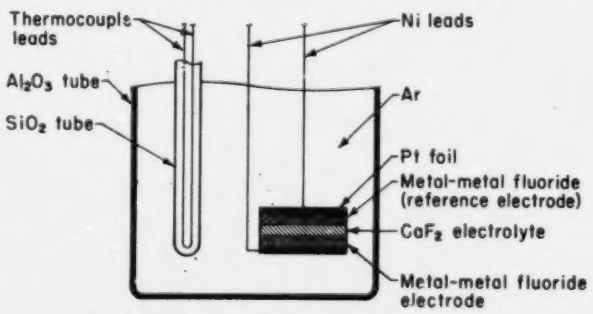

FIGURE 1. - High-temperature galvanic cell.

[2]Underlined numbers in parentheses refer to items in the list of references at end of this report.

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TABLE 1. - Impurities[1] detected in reagents

Reagent and impurity elements	wt pct	Reagent and impurity elements	wt pct	Reagent and impurity elements	wt pct
Mn:		Ni:		CoF_2:	
Al.....	0.07	Co.....	0.045	Al.....	0.02
Ca.....	.02	NiF_2:		Ca.....	.27
Mg.....	<.03	Co.....	.032	Mg.....	.02
Ni.....	.03	Cu.....	.021	Mn.....	.07
Si.....	.17	Co:		Ni.....	.21
MnF_2:		Ni.....	.09	Si.....	.07
Ca.....	.1				

[1]Impurities not detected by spectrochemical analyses, except as noted in the table, were Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hf, Li, Mg, Mn, Na, Ni, P, Pb, Pd, Pt, Sb, Si, Sn, Ta, Ti, V, W, Y, Zn, and Zr.

Electrodes were prepared by blending and compacting 1:1 molar mixtures of nickel, manganese, or cobalt with their respective coexisting fluorides NiF_2, MnF_2, or CoF_2. Pellets, 9 mm in OD by 3 mm thick, were formed in a steel die under a pressure of 210 MPa. Compacts of the metals and their coexisting fluorides were sintered in ultra-high-purity argon at 1,000 K for approximately 30 h. The surfaces of the sintered compacts were polished and fitted against a single crystal of CaF_2, 10 mm in OD and 3 mm thick. Assembled cells were purged with 20 cm^3/min of argon and operated under a positive pressure of approximately 30 Pa. Cells were heated to 900 K and permitted to stabilize for 16 h. Emf measurements were made with a Keithley[3] model 642 high-input-impedance digital electrometer. Measurements were completed during the first day following a preliminary 16-h stabilization period. Cell response to temperature change was rapid, and potentials stabilized within 0.5 h after a steady-state temperature was obtained. Reversibility of the cell reactions was checked by approaching equilibrium from temperatures above and below a specified temperature. Reproducibility was checked by obtaining measurements from several cells for each determination. The cell was shielded from electric field effects in the high-impedance circuit by placing a grounded nickel shield around the cell. The cell was dismantled after completion of the experimental measurements, and the electrodes were removed for phase identification and lattice parameter measurements. There was no visible corrosion of the platinum contacts with the electrodes. X-ray analyses confirmed the products and reactants for the cell reactions and showed that intersolubility of the two-phase electrode mixtures was negligible.

RESULTS AND DISCUSSION

MnF_2

The standard Gibbs energy formation, $\Delta Gf°$, of MnF_2 was determined by measuring the open-circuit potentials for the reversible cell

Ni, Pt, Mn, MnF_2//CaF_2//NiF_2, Ni, Pt, Ni

with the overall cell reaction

$$Mn(c) + NiF_2(c) = MnF_2(c) + Ni(c). \quad (2)$$

Results of these measurements are reported in table 2. Representative emf-versus-temperature data are illustrated in figure 2. A standard Gibbs energy formation of MnF_2 was derived from the relationship

$$\Delta G°(\text{reaction } 2) = -nFE = \Delta Gf°(MnF_2) - \Delta Gf°(NiF_2). \quad (3)$$

[3]Reference to specific trade names does not imply endorsement by the Bureau of Mines.

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TABLE 2. - Emf (E) of cell and thermodynamic properties of MnF_2

Experiment	Temperature, K	Emf (E), mV[1]	$-\Delta Gf°(MnF_2)$, cal/mol	$-\Delta Hf°_{298}(MnF_2)$, cal/mol
1.....	745.7	1,093.15	179,688	204,330
2.....	768.4	1,095.85	178,994	204,349
3.....	769.4	1,095.45	178,939	204,326
4.....	790.8	1,099.55	178,351	204,408
5.....	792.0	1,100.25	178,345	204,439
6.....	813.6	1,102.85	177,685	204,458
7.....	814.1	1,103.05	177,676	204,464
8.....	834.3	1,105.85	177,076	204,501
9.....	835.8	1,105.95	177,027	204,500
10.....	856.4	1,108.55	176,403	204,523
11.....	856.7	1,108.15	176,373	204,502
12.....	906.4	1,115.65	174,925	204,609
13.....	909.8	1,119.15	174,963	204,753
14.....	932.6	1,122.25	174,284	204,784
15.....	934.0	1,121.95	174,220	204,764
16.....	934.9	1,122.75	174,223	204,795
17.....	956.8	1,125.45	173,073	204,327
18.....	958.2	1,125.65	173,516	204,812
19.....	959.9	1,125.45	173,446	204,795
20.....	981.0	1,128.95	172,845	204,848
21.....	982.8	1,128.55	172,762	204,821
22.....	1,004.7	1,132.45	172,151	204,888
23.....	1,006.6	1,130.15	171,977	204,773
24.....	1,028.6	1,133.35	171,330	204,807
25.....	1,031.1	1,133.25	171,249	204,772
26.....	1,052.7	1,136.55	170,608	204,830
27.....	1,078.3	1,141.05	169,891	204,902
Average.....	NAp	NAp	NAp	[2]204,633±196

NAp Not applicable.

[1]Average of 2 measurements (±0.05 mV) taken at 20-min intervals.

[2]Error from these measurements corresponds to a standard deviation; precision uncertainty is ±392 cal/mol; overall accuracy is ±560 cal/mol.

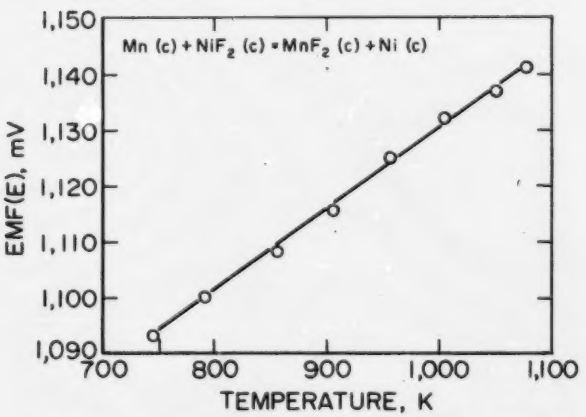

FIGURE 2. - Emf (E) versus temperature for MnF_2 cell.

The values of $\Delta Gf°(NiF_2)$, obtained by interpolation of data reported in a compilation (13) and the values of E listed in table 2, were substituted in equation 3 to derive $\Delta Gf°(MnF_2)$ for each temperature. The results are listed in column 4 of table 2.

The values for $\Delta Hf°_{298}(MnF_2)$, listed in the fifth column of table 2, were obtained by the third-law method as described in the literature (14), using the Gibbs energy function, $Gef \equiv \{G°(T) - H°(298)\}/T$, listed in the literature (15-17) and substituting $\Delta Gf°(MnF_2)$ for each temperature into the following identity corresponding to $Mn(c) + F_2(g) = MnF_2(c)$:

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$$\Delta Gef \equiv \Delta\{G°(T) - H°(298)\}/T$$

$$\equiv \{\Delta Gf°(T) - \Delta Hf°(298)\}/T. \quad (4)$$

The values of Gef and ΔGef for the formation reaction Mn(c) + F_2(g) = MnF_2(c) are listed in table 3. The value of ΔGef for each temperature in table 2 was calculated by interpolation or short extrapolation of the values in table 3. $\Delta Hf°_{298}$ of MnF_2 for each temperature was derived by rearranging equation 4 and substituting the values of $\Delta Gf°(MnF_2)$ that are listed in column 4 of table 2 and the interpolated values of ΔGef from table 3. The average of all values for $\Delta Hf°(MnF_2)$ is −204,633±196 cal/mol. The standard deviation of ±196 cal/mol refers to the present measurements in table 2. Additional errors and uncertainties are those associated with the thermal quantities involved in the calculations. For example, the uncertainty in $\Delta Gf°(NiF_2)$ is ±400 cal/mol (13). The overall uncertainty of $\Delta Hf°_{298}$ was derived by obtaining the square root of the sum of the squares of the uncertainty from these measurements (±392 cal/mol) and the uncertainty in $\Delta Gf°(NiF_2)$ of ±400 cal/mol to yield

$$\Delta Hf°_{298}(MnF_2) = -204,633\pm560 \text{ cal/mol}. \quad (5)$$

A least squares treatment of the data for E fitted to an equation linear in T and extrapolation to 298.15 K by a second-law method yields $\Delta Hf°_{298}(MnF_2)$ = −204,626±560 cal/mol. Agreement with equation 5 is good; however, the recommended value is that based on the third-law method.

Combination of equation 5 from the present investigation with the tabulated data from the literature (15-17) yields, from the results of the third-law method (14),

$$\Delta Gf°(MnF_2) = (-203,008 + 30.96T)\pm560 \text{ cal/mol}$$

$$(745.7\text{-}1,078.3 \text{ K}) \quad (6)$$

for the reaction Mn(c) + F_2(g) = MnF_2(c). The constants in equation 6 are ΔH° = −203,008 and ΔS° = −30.96. Both constants refer to 912 K, the midpoint in the temperature range 745.7 to 1,078.3 K of this investigation; however, both terms remain fairly constant, and within experimental errors, equation 6 may be used to express $\Delta Gf°(MnF_2)$ for the entire range of these measurements. A similar study (5) for reaction 2 reported

$$\Delta Gf°(MnF_2) = -197,000 + 22.28T \text{ cal/mol}$$

$$(732\text{-}1,071 \text{ K}). \quad (7)$$

Results of another electrochemical investigation (18) for the cell reaction $3MnF_2$(c) + 2Al(c) = $2AlF_3$ + 3Mn(c) were expressed as

$$\Delta Gf°(MnF_2) = -204,120 + 32.77T \text{ cal/mol}$$

$$(740\text{-}820 \text{ K}), \quad (8)$$

and a third-law value for the enthalpy of formation was reported as

$$\Delta Hf°_{298}(MnF_2) = -205,400\pm1,000 \text{ cal/mol}. \quad (9)$$

Comparison of equations 7 and 6 shows considerable difference in the constants ΔH° and −ΔS°. Agreement between equations 8 and 6 is better; however, equation 8 is valid for the narrow temperature range of 740 to 820 K, whereas the present investigation was conducted over a wider temperature range of 745.7 to 1,078.3 K.

TABLE 3. - Auxiliary thermodynamic data for MnF_2 reaction

Temperature, K	-Gef, cal/mol			ΔGef, cal/mol
	Mn(c) (15)	F_2(g) (15)	MnF_2(c) (16-17)	
700.....	9.547	50.648	27.0529	33.1421
800.....	10.130	51.303	28.5025	32.9305
900.....	10.700	51.936	29.8756	32.7604
1,000...	11.264	52.537	31.2100	32.5910
1,100...	11.854	53.111	32.5300	32.4350

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CoF_2

The standard Gibbs energy of formation of CoF_2 was determined by measuring the open-circuit potential for the cell

Ni, Pt, Co, CoF_2//CaF_2//NiF_2, Ni, Pt, Ni

with the overall cell reaction

$$Co(c) + NiF_2(c) = CoF_2(c) + Ni(c). \quad (10)$$

Potential measurements for reaction 10 are listed in table 4. Representative emf-versus-temperature data are illustrated in figure 3. A standard Gibbs energy of formation of CoF_2 can be derived from the relationship

$$\Delta G°(\text{reaction 10}) = -nFE = \Delta Gf°(CoF_2) - \Delta Gf°(NiF_2). \quad (11)$$

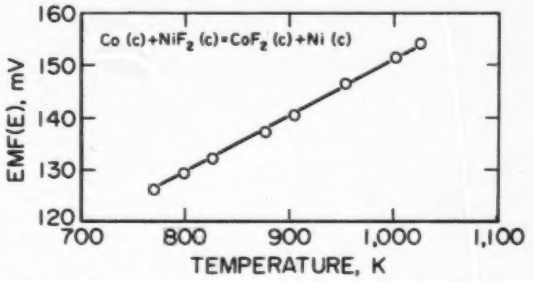

FIGURE 3. - Emf (E) versus temperature for CoF_2 cell.

Values of $\Delta Gf°(NiF_2)$, obtained by interpolation from a compilation (13) and values of E in table 4, were substituted in equation 11 to derive $\Delta Gf°_{298}(CoF_2)$ at each temperature, as listed in the fourth column of table 4.

The third-law values of $\Delta Hf°_{298}(CoF_2)$ were derived in a similar manner to that described for MnF_2 and are listed in the fifth column of table 4. Values of Gef at several temperatures intervals for Co

TABLE 4. - Emf (E) of cell and thermodynamic properties of CoF_2

Experiment	Temperature, K	Emf (E), mV[1]	$-\Delta Gf°(CoF_2)$, cal/mol	$-\Delta Hf°_{298}(CoF_2)$, cal/mol
1.....	769.5	126.65	134,252	161,021
2.....	798.1	129.55	133,354	161,053
3.....	826.0	132.35	132,475	161,082
4.....	852.4	132.85	131,545	161,007
5.....	878.5	138.45	130,862	161,164
6.....	879.3	138.95	130,856	161,184
7.....	904.1	140.85	130,048	161,172
8.....	904.5	139.95	129,989	161,129
9.....	905.0	140.55	130,002	161,155
10.....	905.3	141.95	130,056	161,218
11.....	929.7	143.15	129,230	161,174
12.....	930.0	144.55	129,265	161,219
13.....	930.3	143.45	129,222	161,187
14.....	930.7	143.05	129,190	161,166
15.....	954.7	146.75	128,493	161,234
16.....	955.0	145.85	128,442	161,193
17.....	955.1	145.05	128,401	161,155
18.....	955.1	145.15	128,406	161,160
19.....	978.5	149.35	127,754	161,252
20.....	979.0	148.15	127,681	161,195
21.....	979.3	147.35	127,633	161,156
22.....	1,002.7	151.75	126,991	161,256
23.....	1,026.8	154.35	126,242	161,276
Average.....	NAp	NAp	NAp	[2]161,166±69

NAp Not applicable.

[1]Average of 2 measurements (±0.05 mV) taken at 20-min intervals.

[2]Error from these measurements corresponds to a standard deviation; precision uncertainty is ±138 cal/mol; overall accuracy is ±420 cal/mol.

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(15), F_2 (15), and CoF_2 (19), and ΔGef for the reaction $Co(c) + F_2(g) = CoF_2(c)$ are given in table 5. $\Delta Hf^\circ_{298}(CoF_2)$ for each temperature was derived by rearranging equation 4 and substituting the interpolated values of ΔGef from table 5 and the values of $\Delta Gf(CoF_2)$ that are listed in table 4. The average value of $\Delta Hf^\circ(CoF_2)$ is −161,166±69 cal/mol. The standard deviation of ±69 cal/mol refers to the present measurements listed in table 4. Additional errors and uncertainties are associated with the various thermal quantities involved in the calculation. For example, the uncertainty for $\Delta Gf^\circ(NiF_2)$ is ±400 cal/mol. Combination of these errors with the uncertainty of ±138 cal/mol (2 × 69) from the present measurements yields

$$\Delta Hf^\circ_{298}(CoF_2) = -161,166\pm420 \text{ cal/mol.} \quad (12)$$

A least squares treatment of the data for E fitted to an equation linear in T and extrapolation to 298.15 by a second-law method yields $\Delta Hf^\circ(CoF_2)$ = −161,148±420 cal/mol. Agreement with equation 12 is good; however, the recommended value is from equation 12, based on the third-law method.

TABLE 5. – Auxiliary thermodynamic data for CoF_2 reaction

Temperature, K	-Gef, cal/mol			ΔGef, cal/mol
	Co(c) (15)	F_2(g) (15)	CoF_2(c) (19)	
700.....	8.961	50.648	24.627	34.982
800.....	9.530	51.303	26.131	34.702
900.....	10.076	51.936	27.576	34.436
1,000...	10.596	52.537	28.954	34.179
1,100...	11.116	53.111	30.265	33.962

Combination of equation 12 with the tabulated data (16, 19) using the results for the third-law method yields

$$\Delta Gf^\circ(CoF_2) = (-159,090 + 32.13T)\pm420 \text{ cal/mol}$$

$$(769.5\text{-}1,026.8 \text{ K}) \quad (13)$$

for the reaction $Co(c) + F_2(g) = CoF_2(c)$. The constants in equation 13 are ΔH° = −159,090 and ΔS° = −32.13. Both constants refer to 898 K; however, they vary only slightly with temperature. Within experimental errors, equation 13 may be used to express ΔG° for the indicated range of temperature.

A compilation (19) based on gas-phase equilibration studies reported ΔHf°_{298} = −160,200±1,000 cal/mol, which compares favorably with −161,166±420 cal/mol from this investigation. Similar emf studies (5, 20) for reaction 10 reported the following results:

$$\Delta Gf^\circ(CoF_2) = -163,000 + 34.17T \text{ cal/mol}$$

$$(581\text{-}1,066 \text{ K}) \quad (14)$$

and $\Delta Gf^\circ(CoF_2)$

$$= (-158,542 + 32.37T)\pm600 \text{ cal/mol}$$

$$(850\text{-}1,050). \quad (15)$$

Comparison of equation 14 with the present results expressed by equation 13 shows considerable difference in both constants (ΔH° and $-\Delta S^\circ$). Equation 15 agrees favorably with the results from this investigation as expressed by equation 13.

SUMMARY AND CONCLUSIONS

Standard Gibbs energies of formation of MnF_2 and CoF_2 were determined by emf measurements from reversible high-temperature galvanic cells using CaF_2 as the electrolyte. Third-law analyses of the present data yield standard enthalpies of formation

$$\Delta Hf^\circ_{298}(MnF_2) = -204,633\pm560 \text{ cal/mol}$$

and $\Delta Hf^\circ_{298}(CoF_2) = -161,166\pm420$ cal/mol.

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